PHENOXY HERBICIDE RESIDUES AND THEIR PERSISTENCE

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**Title:** Herbicide Chemicals that are Persistent and those that are rapidly decomposed are of value in the many facets of agriculture, forestry, range, and water management practice. It would be easy for the layman to conclude that persistence of herbicidal chemicals is undesirable, but that is not necessarily so. Advantage can be taken of long-term persistence in the treatment of areas where long term control of vegetation is needed.

**Keywords:**
- Clorophenoxy Acid Residues
- Herbicide Residue Problems
- Herbicide Applications
- Herbicide Chemicals
- Residues in Water

**Abstract:**
Herbicide chemicals that are persistent and those that are rapidly decomposed are of value in the many facets of agriculture, forestry, range, and water management practice. It would be easy for the layman to conclude that persistence of herbicidal chemicals is undesirable, but that is not necessarily so. Advantage can be taken of long-term persistence in the treatment of areas where long term control of vegetation is needed.
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PHENOXY HERBICIDE RESIDUES AND THEIR PERSISTENCE

by
W. B. House, L. H. Goodman, H. M. Gadberry
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SUMMARY

1. Herbicide chemicals that are persistent and those that are rapidly decomposed are of value in the many facets of agriculture, forestry, range, and water management practice. It would be easy for the layman to conclude that persistence of herbicidal chemicals is undesirable, but that is not necessarily so. Advantage can be taken of long-term persistence in the treatment of areas where long term control of vegetation is needed in orchards, parking lots, industrial plant installations and rights-of-way. On the other hand, the accumulation and persistence of herbicidal residues in soils, plant vegetation and water pose certain problems or hazards.

INTRODUCTION

2. Herbicide Residue Problems. Injury to sensitive crops that are grown in rotation and to subsequent natural vegetation may result from herbicide residues. Accumulation of herbicide residues in foliage, seed, berries and fruit consumed as food by animals, birds, fish may pose a problem to the human health. Leaching of herbicides into streams, lakes and reservoirs which would affect aquatic life and water quality for human use.
consumption are also a problem for widespread use. Residues and persistence of herbicides are reviewed under the general categories of soil, vegetation and water. The subject of residues and persistence of herbicidal residues has been reviewed in depth by Audus (1960), Audus (1964), and Sheets and Harris (1965).

III. SOILS

3. Chlorophenoxy Acid Residues. Some of the earliest work on the persistence of chlorophenoxyacetic acids and their esters was undertaken by DeRose (1946) and Allard and DeRose (1946). DeRose and Newman (1947) made comparisons with 2,4-D, 2,4,5-T and MCPA in greenhouse and field tests. The germination of soybeans was used as a bioassay. The rates of application of compounds varied from 1 to 12.5 mg/lb of soil. In the greenhouse test, the 2,4-D persisted for 67 days and the 2,4,5-T at the 1 mg level persisted for 147 days and it was still high at 11 months. In the field evaluations, they applied from 5 to 20 lb/acre and the 2,4-D and the MCPA rapidly disappeared while the 2,4,5-T persisted for 93 days. The findings for 2,4-D were essentially the same as those reported by Newman and Thomas (1949) and Hernandez and Warren (1950) and for 2,4-D and 2,4,5-T by Newman, Thomas and Walker (1952).

a. Obviously, there are a number of factors that are involved in persistence and these tests indicated that the temperature and the moisture of the soil was highly important. This could be correlated
with the approach to the optimal conditions for the action of soil microorganisms. The subject of the mechanisms that are involved in the reduction of herbicidal activity will be discussed in some detail in a later section.

b. Sheets and Harris (1965) determined that the residual phytotoxicity for 2,4-D in greenhouse tests lasted about one month, even when the rate of application was raised to 40 lb/acre. On the other hand, in field tests, a 5-lb. application persisted for 1 month. In the greenhouse 2,4,5-T persisted for one month at the 4-lb. level, but when 2,4,5-T was used in field tests at 5 lb/acre, it existed for 3 months. 2,4-D, regardless of application rate, persists about 1 month, 2,4,5-T is more persistent in that it appears to remain in the soil up to 3 months. Low moisture conditions, low temperature and difference in soil types extends the period of persistence.

c. Norris (1966) and Norris and Greiner (1967) have reported some studies of persistence of 2,4-D and 2,4,5-T in forest litter when triethanol amine salts of labeled 2,4-D and 2,4,5-T were applied in water to the surface of the litter at a rate of 2 lb. acid equivalent per acre. The following observations were made--percent of degradation as measured by radioactive CO₂ liberation:

\[
\begin{array}{ccc}
\text{315 Hr} & \text{690 Hr} \\
2,4-D & 89\% & -- \\
2,4,5-T & 23\% & 53\%
\end{array}
\]

Norris felt that the slower rate of decomposition of the 2,4,5-T may have been due to a lag in accommodation of microorganisms to the chemical.
d. In another study, forest litter was selected from five types of forest trees: Douglas fir, big leaf maple, vine maple, Ceanothus and red alder. These little samples were treated with 3 lb/acre equivalent of (1) 2,4-D acid, (2) triethanolamine salt, (3) isoocytI ester, (4) isoocytI ester plus 1 lb/acre of DDT or (5) isoocytI ester plus 6 gal/acre diesel oil. In 15 days, the recovery of 2,4-D applied as the salt varied from 60 to 70% for all the types of litter. The esters persist longer than the acid, 65% vs. 55%. The addition of 1 lb of DDT/acre seemed to stimulate herbicidal degradation.

IV. VEGETATION

4. Herbicide applications for crop lands can be divided into three types: (1) pre-plating, (2) pre-emergence, (3) post-emergence. A number of factors have to be considered in the selection of a herbicide for a specific crop use: weed specificity, fairly rapid dissipation and minimum residue carry-over when crops are rotated. Certainly, weather conditions have an effect on herbicide dissipation and the tolerance of the primary and the succeeding crop to possible soil residues, enters into the picture.

a. Crafts (1964) has summarized the literature on the metabolism of the phenoxy acids in plants. Some specific examples taken from this review are as follows: 2,4-D is not freely mobile in the plant; therefore, it is not easily translocated to the roots (Crafts, 1959). In addition, 2,4-D is readily oxidized in plant tissues.
b. Luckwill and Lloyd-Jones (1960 a,b) worked with the metabolism of 2,4-D in berries. Red currant oxidized up to 50% of the carboxyl and 20% of the ethylene carbon of 2,4-D when it was supplied to the leaves for seven days through cut petioles. In contrast, the black currant is susceptible to 2,4-D, oxidizing only 2% of the chemical under the same conditions. The red currants were able to metabolize 2,4,5-T, 4 CPA and MCPA.

c. The Cox apple variety is resistant, decarboxylating 50% of the applied 2,4-D in 92 hours. Bramley’s seedling apple, metabolized about 2%. It has been reported that stored lemons in which 2,4-D had been added to the oranges, Erickson and Field (1962) found that orange trees sprayed with 22 ppm of 2,4-D contained an average of 0.1 ppm of 2,4-D one day after spraying.

d. Morton (1966) studied the absorption and distribution of 2,4,5-T in mesquite (Prosopis juliflora var. glandulosa (Torr) Cockerel) seedlings. Absorption took place throughout a 72-hour period. At 72 hr, the recovery of absorbed 2,4,5-T as measured by radioisotope techniques, from all untreated tissues was 12, 13 and 3% at 70, 85 and 100°F, respectively. The distribution and residue of labeled 2,4,5-T in red maple and white ash has been investigated by Leonard et al. (1966). When 2,4,5-T ester or amine is applied to leaves of these species, 30 days after treatment 96-99% of the C^{14} was found in the leaf laminas. When these compounds were applied to bark (stem) the 2,4,5-T amine was translated less than the ester form. The ester in amounts of up to 24%, moved to the leaf laminas.
e. 2,4-D is especially harmful to dicotyledonous plants: tomatoes, cotton and some legumes. It has been reported by Monroe (1964) that 1 oz. of 2,4-D distributed over 35 acres of cotton will seriously injure the crop. This work was done by Dunlap and Engle (1949) at the Texas Agricultural Experimental Station.

f. Legume crops, while not as sensitive as cotton, are generally receptive to 2,4-D action. Four pounds per acre will kill ladino, white clover and lespedeza. The tolerance of peanuts to 2,4-D is generally 1-1/2 lb/acre. Soybeans seem to be tolerant to 2,4-D up to 2 lb/acre. Rice tolerates 1/2 lb/acre. Pasture plants tolerate 1 lb/acre and sorghum is tolerant to 1-1/2 lb/acre. When soybeans are treated with 1/2 to 1 lb/acre of the amine formulation of 2,4-D, the mature seed will accumulate and retain a small residue of 2,4-D (Szabo, 1965).

g. Monroe (1964) also reported on some unusual observations occurring after 2,4-D treatment. Corn treated with 2,4-D becomes more palatable for field mice and sheep will eat Centaurea Salsalititia only after it is sprayed with 2,4-D.

f. There have been a few reports of residues in pasture grasses that are related to the transfer to the milk of cows grazing on these crops. Pastures have been sprayed since 1945 and in 1962 over 4 million acres were sprayed with various amine salt and ester formulations of 2,4-D. Klingman et al. (1966) found that residues in pasture grasses sprayed with the butyl ester of 2,4-D disappeared more rapidly than in those from pastures sprayed with 2-ethylhexyl ester. Virtually all of the butyl ester of 2,4-D is hydrolyzed to the acid within 1/2 hr after spraying. This is contrasted to 12 ppm of residue remaining after
spraying with the 2-ethylhexyl ester of 2,4-D, and appreciable amounts persisted for 7 days. The transfer of 2,4-D to milk is insignificant. Residues less than 0.01 ppm, 2,4-D in milk would be found if dairy cows are not pastured for 7 days after spraying with the butyl or 2-ethylhexyl ester of 2,4-D.

V. WATER RESOURCES

5. Residues in Water. One of the real problems from the standpoint of the effect of herbicide residues and the persistence of these residues in the ecosystem involves water supplies for human consumption. Watersheds and drainage from cropped areas that have been treated with herbicides might in turn result in secondary effects involving the health of domestic animals, wildlife or aquatic life. Nicholson and Thomas (1965) have estimated that the present population depending upon surface streams for drinking water in 1960 was about 100,000,000 which was up 15% over 1940. It is estimated by 1980 that the population depending upon surface water would be about 165,000,000 out of 200,000,000. With increasing use of herbicides on noncropland, it is important to evaluate their persistence in surface water. Most of the work that has been reported has been concerned with the phenoxyacetic acids and their esters, paraquat, diquat, silvex and amitrole.

a. Faust, Tucker and Aly (1961) and Faust and Aly (1963) investigated the effect of 2,4-D and 2,4-dichlorophenol (2,4-DCP) on drinking water quality. 2,4-DCP can occur as a formulation impurity or as a product of chemical or biological degradation of 2,4-D in surface water.
At concentrations less than 70 ug/liter and 2 ug/liter, respectively, chlorinated phenols impart objectionable medicinal taste and odors to water. They found levels of 2,4-DCP ranging from 70 to 4500 ug/g of formulation. In laboratory carboy studies with lake water, using two granular forms of 2,4-D, 9.5 and 16.7 ug/liter of 2,4-DCP were released in 7 days. Maximum concentrations of 14.7 and 20.7 ug/liter were observed at 148 and 218 days. In other carboy tests, they found that the phenol disappeared rapidly under conditions of neutral and stable pH values, aeration and small amounts of organic matter. About 40 to 50% of 2,4-dichlorophenol can persist up to 80 days under conditions of acid pH and anaerobic surface water unfavorable for biological oxidation. They suggested that there was a possibility of three mechanisms being responsible for the release of free phenols from 2,4-D and 2,4,5-TP herbicides: "(1) a free phenol impurity present in the formulation as a result of manufacturing process, (2) chemical hydrolysis of the organic ester in water, (3) biological degradation of the ester portion of the herbicides."

b. Cochrane et al. (1967) evaluated the persistence of Kuron.1/ When the herbicide was applied to the surface water at the rate of 8 lb. equivalent acid per acre, they obtained a rapid hydrolysis of the esters to silvex acid. Silvex acid gradually diminished in concentrations and traces remained for at least 19 weeks. These authors recommended

1/ 64.5% propylene glycol butyl ether esters of silvex equal to 42.8% silvex acid equivalent.
that silvex should not be applied to a body of water that is being used as a source of water for human consumption.

c. Since surface water accounts for most of the municipal water supplies, our attention is drawn to the spraying of forest lands over watersheds with herbicides. According to Shepherd et al. (1966), about 71 million acres in the U. S. were sprayed with weed control chemicals in 1962. About 4% of the total acres thus treated, or 2.5 million acres was forest and range land. Tarrant and Norris (1967) have pointed out that about 100,000,000 acres of commercial forest land at the present are either nonstocked or poorly stocked with trees of acceptable quality or species. However, these forests received about one-half the total precipitation and yield about three-fourths of the total stream flow. Most forest lands annually receive an average of 45 inches of precipitation, which is about twice that which falls on other lands, and forest lands yield about 20 inches of run-off, which is almost seven times that of other lands.

d. Periodic sampling in Oregon revealed only a light and short-lived contamination of stream water as a result of aerial spraying of 2,4-D and 2,4,5-T. In a test reported by Gratekowski et al. (1965) and Tarrant and Norris (1967) detectable quantities of herbicides were found in virtually all streams sampled after 2,4-D, 2,4,5-T or a 1 to 1 mixture of 2,4-D and 2,4,5-T low volatile esters in diesel oil were applied at the rates of about 2 lb/acre from a helicopter. The quantities found range from 0.2 ppb to 70 ppb. Usually in a matter of days, the level fell to 0.2 ppb. Maximum variation from checkpoint to checkpoint was

1/ Unpublished information
a total disappearance of 2,4-D in two days and at another, 17 days. Krammes and Willets (1964) reported on the spraying of sprouted vegetation after a watershed was cleared with equal parts of 2,4-D and 2,4,5-T in diesel oil. They used 89 gal of herbicides (concentration of acid equivalent wasn't reported) in this application and later they stumpsprayed with 45 gal of herbicide. They took samples over a five-month period; all samples were below 1 ppm and no trace of diesel oil was found. In another study, brush was sprayed by helicopter to try to convert vegetation on a steep side slope from bush to grass. They applied 3/4 gal of 3 lb acid equivalent each of low volatile esters of 2,4-D and 2,4,5-T in 1 gal of diesel oil and 17-1/2 gal of water. They used 20 gal of this mixture per acre. As a follow-up treatment, they hand sprayed the brush with a herbicide mixture of 1/2 gal of 2 lb acid equivalent each of 2,4-D and 2,4,5-T in 1 gal of diesel oil and 98 gal of water. They sampled the surface water at weirs and for all practical purposes, no herbicides were found. In sampling the soil, they detected small amounts of herbicides at 8 days. There were no herbicides present a month and a half after initial spraying.

e. When 2,4-D and 2,4,5-T combinations were used in a 1 to 1 basis and at the rate of 2 lb/acre, in 9-1/2 gal of diesel oil, there is no effect upon salmon fry or on stream bottom organisms (Tarrant and Norris, 1967).

f. Evidently diesel oil used in the sprays is not a source of trouble. Norris cites work by Linden and Müller (1963), who applied
diesel oil at rates in excess of 50, 250, and 500 gal/acre, which was followed by leaching with 100 ml of rainwater and only 1.5 to 2 ppm of diesel oil were found in sandy loam at a depth below 2-1/2 inches. These investigators felt that the application of diesel oil to the soil surface at rates of more than 50 gal/acre presented no threat to ground water quality.

g. The waterhyacinth is a pest in southern streams and a considerable amount of work has been done in removing these plants by mechanical and chemical methods. There is a great deal of interest in the persistence of herbicides in these waters because of the possibility of carryover into the Gulf Coast areas which support shell fish life. Averitt (1967) investigated the rates of disappearance of 2,4-D acid equivalent dispersed at 4 lb/acre by injecting the herbicide into the propeller wash of a small motor boat. On the first day, the concentration was about 689 ppb and had fallen on the 4th day to 80 ppb. The decline thereon was rather slow until the 31st day, when it had dropped to 10 ppb. They also conducted some tests in plastic boxes with applications of 5 lb/acre of 2,4-D. Twenty-two days were required for the concentration to drop from a high on the seventh day of 972 ppb to 11 ppb. Aly and Faust (1964) made studies of the decomposition or persistence of 2,4-D residues in hydrosoils. When the herbicide was added to lake bottom soil that had been treated previously with 2,4-D, the herbicide decomposed at 35 days. When 2,4-D was added to untreated lake hydrosoil, the decomposition time was 65 days. Frank and Comes (1967) worked with
granular 2,4-D (20%). The herbicide persisted longer in the hydrosoil than in the water, but it could not be detected after 55 days.

h. A study of the effect of 2,4-D treated irrigation water on red Mexican beans has been reported by Bruns (1951). When herbicide at 2 lb/acre in the water was applied to beans in the seedling stage, the root systems were severely attacked. Within 16 days the plants began to recover. When the level was raised to 6 lb/acre, the yield was reduced 40%. When these levels of application were made in the bloom stage, the 2-lb. level caused no significant reduction in yield. The loss at 16 lb. was 29%. Frank and Comes (1967) introduced 1.33 ppm of 2,4-D into a pond; one day after treatment the concentration was 0.024 ppm. The maximum, 0.067 ppm, occurred on the 18th day and fell to 0.019 ppm by the 24th day.


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